In situ analysis of major and trace elements of anhydrous minerals by LA-ICP-MS without applying an internal standard

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ARTICLE INFO

ABSTRACT

Here we describe an internal standard-independent calibration strategy for LA-ICP-MS analysis of anhydrous minerals and glasses. Based on the normalization of the sum of all metal oxides to 100 wt.%, the *ablation yield correction factor* (AYCF) was used to correct the matrix-dependent absolute amount of materials ablated during each run.

$$AYCF = \frac{100}{\sum_{j=1}^{N} (cps_{sam}^j \times I^j)}, I^j = C_{rm}^j / cps_{rm}^j,$$ where cps_{sam}^j and cps_{rm}^j are net count rates of analyte element j of the sample and reference material for calibration, C_{rm}^j is concentration of element j in the reference material, N is the number of elements that can be determined by LA-ICP-MS. When multiple reference materials were used for calibration, l value can be calculated with regression statistics according to the used reference materials. Applying an AYCF and using the USGS reference glasses BCR-2G, BHVO-2G and BIR-1G as reference materials for external calibration, analyses of MPI-DING reference glasses generally agree with recommended values within 5% for major elements (relative standard deviation (RSD)=0.3–3.9% except for P_2O_5, $n=11$), and 5–10% for trace elements. Analyses of anhydrous silicate minerals (clinopyroxene, orthopyroxene, olivine, plagioclase and garnet) and spinel generally agree with the results of electron microprobe analysis within 0.2–7% for SiO_2, Fe_2O_3, MgO and CaO. RSD are generally <5% for elements with concentrations >0.1 wt.%. The results indicate that, by applying an AYCF and using USGS reference glasses as multiple reference materials for calibration, elements of these anhydrous minerals can be precisely analyzed in situ by LA-ICP-MS without applying internal standardization. The different element fractionations between the NIST glasses and those glasses with natural compositions indicate that NIST SRM 610 is a less than ideal reference material for external calibration of analyses of natural silicates.

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1. Introduction

Many geological, environmental and industrial applications can be enhanced through integrating microbeam and bulk geochemical determinations of major and trace element concentrations (Audétat et al., 1998; Heinrich et al., 2003; Sylvester, 2006; Steely et al., 2007). Advantages of in situ microanalysis include minimal sample preparation, low blank, information about the spatial distribution of compositional characteristics and the ability to avoid microscopic inclusions of foreign material. Previous comparative studies have emphasized the utility of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) as a quantitative microbeam technique capable of rapid and precise determinations of sub-ppm trace element concentrations in a variety of targets (Horn et al., 1997; McCandless et al., 1997; Nesbitt et al., 1997; Günther et al., 1998; Jorge et al., 1998; Norman et al., 1998; Mason et al., 1999; Reid et al., 1999; Gao et al., 2002; Guillong et al., 2005; Kurosawa et al., 2006; Jochum et al., 2007).

For LA-ICP-MS analysis, the absolute amount of materials ablated during each run varies from one to another due to differences in the sample matrix and the related absorption behaviour of the wavelength used for ablation (e.g., Hemmerlin and Mermet, 1996; Horn et al., 2001). An internal standard is generally used to correct the variations in the absolute amount of materials ablated during each run (Longerich et al., 1996). In other words, the concentration of at least one element must be known or determined by an independent method prior to LA-ICP-MS analysis. For metals or chemically simple minerals (e.g., quartz, rutile, zircon, fluorite or sapphire), the internal standard can be determined according to their constant stoichiometry (Anczkiewicz et al., 2001; e.g., Gagnon et al., 2003; Yuan et al., 2004; Zong et al., 2006). However, for most silicate minerals (e.g., olivine, pyroxene, garnet), the elements used as internal standards (e.g., Si, Mg, Ca) can vary widely and are generally determined by electron

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microprobe (EMP). However, electron microprobes are very expensive and not all laboratories have access to them. This hampers the ready application of LA-ICP-MS.

Leach and Hieftje (2000) explored a summed-spectrum normalization calibration procedure to determine elements in alloys by LA-ICP-MS without applying internal standardization. In this method, a normalization factor is computed from the summed signal generated by all sample constituents (Leach and Hieftje, 2000; Leach and Hieftje, 2002; Latkoczy et al., 2005). The total sum of signal normalization technique requires that all analyzed elements have almost the same sensitivity to get accurate results. Although this technique is probably feasible for alloys, it is not practical for silicate minerals with a variable matrix. Regardless of the outcome of the sum normalization calibration procedure, the work of Leach and Hieftje (2000) rekindled an interest in major and trace element analyses of solid materials using LA-ICP-MS without internal standardization. As an improvement to the summed signal normalization technique, Halicz and Günther (2004) calculated the concentration of the internal standard based on normalization of the sum of all metal oxides to 100 wt.% to determine the trace element compositions of anhydrous silicates, and Guillong et al. (2005) normalized concentrations of all elements as oxides to 100 wt.% after external calibration against reference glasses.

For quantitative calibration, the NIST synthetic glasses SRM 612 and SRM 610 have been used as reference materials in most geological LA-ICP-MS analyses (Eggins et al., 1998b; Gao et al., 2002; Eggins, 2003; e.g., Günther et al., 1997; Mason et al., 1999; Guillong et al., 2005; Jochum et al., 2005; Kurosawa et al., 2006). These two reference glasses have the advantage that the concentrations of all trace elements are similar and high enough (~50 ppm and ~500 ppm, respectively) for a precise primary calibration (Pearce et al., 1997; Rocholl et al., 1997). The drawback to the NIST glasses is that their major element composition is very different from any geological matrix, which may lead to significant analytical biases due to matrix effects (e.g., Hinton, 1995; Jochum et al., 2007). Moreover, some compositional heterogeneities have been shown to affect at least twenty four of the doped trace elements in the NIST glasses (Hinton, 1999; Eggins and Shelley, 2002). Therefore, several sets of homogeneous reference glasses of natural compositions, such as the USGS and MPI-DING glasses have been prepared (Rocholl, 1998; Jochum et al., 2000; Guillong et al., 2005; Jochum et al., 2005; Jochum et al., 2006). However, these glasses with natural compositions are mostly used as secondary standards because the natural abundances of some trace elements are too low to permit a precise calibration. To remedy the drawback of natural compositions, four synthetic reference glasses (GSA-1G, GSC-1G, GSD-1G and GSE-1G) have trace element concentrations ranging from less than 1 ppm to 500 ppm have been produced by Stephen A. Wilson at the USGS laboratories (Guillong et al., 2005; Jochum et al., 2005; Jochum and Willbold, 2006). On the other hand, as a complement/improvement, liquid calibration (Halicz and Günther, 2004) were combined with re-normalization to 100 wt.% of all elements expressed as oxides to quantitatively analyze silicates using LA-ICP-MS, which could remedy the drawback of using one standard with natural compositions.

In this study, we show that NIST SRM 610 is not a suitable reference material for external calibration for analysis of natural silicate. Combing summed metal oxide normalization technique and calibration against multiple reference materials with natural compositions, major and trace elements of anhydrous silicate minerals were precisely determined without the need of a single internal standard element.

2. Calibration strategy for LA-ICP-MS

To conduct quantitative analysis by LA-ICP-MS, the relative element sensitivity for each element was usually calibrated using both external calibration (e.g., against the NIST (Pearce et al., 1997), USGS (Jochum et al., 2005) or MPI-DING (Jochum et al., 2006) reference glasses, or synthetic calibration solutions (Halicz and

Günther, 2004)) and internal standardization, as demonstrated by the following Eq. (1) (Longerich et al., 1996).

$$C_{sam}^i = C_{rm}^i \times \left(cps_{sam}^i/cps_{rm}^i\right) \times \left(cps_{rm}^{is}/cps_{sam}^{is}\right) \times \left(C_{sam}^{is}/C_{rm}^{is}\right) \quad (1)$$

where C_{sam}^i = concentration of analyte element i in the sample, C_{rm}^i = concentration of analyte element i in the reference material for calibration, cps_{sam}^i = net count rate (sample signal minus background) of i in the sample, cps_{rm}^i = net count rate of i in the reference material for calibration, cps_{sam}^{is} = net count rate of internal standard element "is" in the sample, cps_{rm}^{is} = net count rate of "is" in the reference material for calibration, C_{sam}^{is} = concentration of "is" in the sample and C_{rm}^{is} = concentration of "is" in the reference material for calibration.

Eq. (1) can be rewritten as the following two equations:

$$C_{sam}^i = C_{rm}^i \times \left(cps_{sam}^i/cps_{rm}^i\right) \times k \quad (2)$$

$$k = \left(cps_{rm}^{is}/cps_{sam}^{is}\right) \times \left(C_{sam}^{is}/C_{rm}^{is}\right). \quad (3)$$

This implies that the quantitative concentration of an element can be obtained once the value of k is known. For a given anhydrous silicate mineral, the sum of all element concentrations expressed as oxides (according to their oxidation states present in the silicates) should be 100 wt.%. In other words, we have the following Eq. (4):

$$C_{sam}^1 + C_{sam}^2 + \cdots + C_{sam}^i + \cdots + C_{sam}^N = 100\,wt.\%. \quad (4)$$

Combining Eqs. (2) and (4) yields the following Eq. (5):

$$k \times [C_{rm}^1 \times (cps_{sam}^1/cps_{rm}^1) + \cdots + C_{rm}^i \times \left(cps_{sam}^i/cps_{rm}^i\right)$$
$$+ \cdots + C_{rm}^N \times (cps_{sam}^N/cps_{rm}^N)] = 100. \quad (5)$$

Eq. (5) can be re-arranged as:

$$k = \frac{100}{\sum_{j=1}^{N} \left(cps_{sam}^j \times l^j\right)} \quad \left(l^j = C_{rm}^j/cps_{rm}^j\right) \quad (6)$$

where N is the number of elements that can be determined by LA-ICP-MS. When multiple reference materials were used for calibration, l value can be calculated with regression statistics derived from the analysis of several reference materials. Therefore, the k value for the sample can be calculated without knowing an internal standard element. Because the absolute value of k calculated from Eq. (6) is a unique factor correcting for change in ablation yield, and thus was named the *ablation yield correction factor* (AYCF) to distinguish it from the k value calculated from Eq. (3) based on one internal standard. Concentrations of all elements can be determined by the following Eq. (7) derived by combining Eqs. (2) and (6).

$$C_{sam}^i = \frac{100 \times cps_{sam}^i \times l^i}{\sum_{j=1}^{N} \left(cps_{sam}^j \times l^j\right)}. \quad (7)$$

However, it should be mentioned that all elements within the matrix need to be determined in this method. In the case of higher concentrations of anions (Cl, F, S and OH) the calibration approach will not provide access to accurate concentrations.

3. Experiments

3.1. Sample preparation

The widely used NIST (SRM 610, 612 and 614) (Pearce et al., 1997), USGS (BCR-2G, BHVO-2G and BIR-1G) (Jochum et al., 2005) and MPI-DING (ATHO-G, GOR128-G, GOR132-G, KL2-G, ML3B-G, StHs6/80-G

and T1-G) (Jochum et al., 2006) reference glasses were used for our experiments. The working values are from the GeoReM database (http://georem.mpch-mainz.gwdg.de/) for the NIST and USGS reference glasses, and from Jochum et al. (2006) for the MPI-DING reference glasses (Table A1 in Appendix). Olivine, orthopyroxene, clinopyroxene, garnet and plagioclase were analyzed to evaluate the capability of analyzing major and trace elements for anhydrous silicate minerals. Spinel was also analyzed for evaluating the potential capability of analyzing other anhydrous minerals. Olivine, orthopyroxene, clinopyroxene and spinel from peridotite were handpicked mineral grains, which were previously analyzed by EMP and solution and laser ablation ICP-MS (Eggins et al., 1998b). Garnet and clinopyroxene from pyroxenite and plagioclase from gabbro were analyzed on thin sections, which were previously analyzed by EMP at the China University of Geosciences. All of the glasses and silicate minerals were cleaned in a 2% HNO_3 bath with ultrasonic washer prior to LA-ICP-MS analysis.

3.2. Instrumentation and operating conditions

LA-ICP-MS analysis was performed at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences. Laser sampling was performed using a GeoLas 2005 System. The laser-generated aerosol was transported from the ablation cell to the ICP-MS instrument using a 1 m transfer tube with an internal diameter of 3 mm. The standard ablation cell in the GeoLas 2005 system is a closed design cell and basically consists of a cylindrical volume of approximately 40 cm^3. An in-house sample mount was placed in the cell, which reduces the effective cell volume to ~14 cm^3. Helium is advantageous as a carrier gas (Eggins et al., 1998a; Günther and Heinrich, 1999) and was thus applied in this study. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. An Agilent 7500a ICP-MS instrument was used to acquire ion-signal intensities. Detailed operating conditions for the laser and the ICP-MS instrument are listed in Table 1. Isotopes that have the least interference were selected for analyses according to the factory-supplied software for most trace elements (Table A1 in Appendix). A few elements (e.g., Ga) were selected according to our experience of solution analyses. For major elements, the less abundant isotopes with the least interference were generally selected for analyses (i.e., ^{29}Si, ^{42}Ca, ^{57}Fe, ^{25}Mg) (Table A1 in Appendix). Interferences of oxides, argides and doubly charged ions on major elements during ICP-MS analysis could impose a serious problem on the accuracy of this method. Thus, the carrier and make-up gas flows were optimized by ablating NIST SRM 610 to obtain maximum signal intensity for ^{208}Pb, while keeping low ThO/Th (0.1–0.3%) and Ca^{2+}/Ca$^+$ ratios (0.4–0.7%) to reduce the matrix-induced interferences as much as possible. The ion-signal intensity ratio measured for ^{238}U and ^{232}Th (NIST SRM 610) (^{238}U/^{232}Th ≈ 1) was used as an indicator of complete vaporization (Günther and Hattendorf, 2005). The calculated fractionation factors (the ratio of the integrated signal obtained for the second 25 s of the continuous ablation to the signal for the first 25 s) (Fryer et al., 1995) using NIST SRM 610 cluster in the range of 0.9–1.1, which implies no significant temporal fractionation within a period of ~50 s (integrated time).

Each analysis incorporates an approximately 20 s background acquisition (gas blank) followed by 50 s data acquisition from the sample. Every 8 sample analyses were followed by two analyses of NIST SRM 610 in order to correct the time-dependent drift of sensitivity and mass discrimination. All analyses were acquired using time resolved software.

3.3. Data calibration

Selection and integration of background and analyte data follow the description by Longerich et al. (1996). Long-term sensitivity drift during ICP-MS analysis is complicated (Cheatham et al., 1993).

Table 1
Typical operation conditions for LA-ICP-MS analysis

ICP-MS conditions	
RF power	1350 W
Plasma gas	14 L min^{-1} Ar
Auxiliary gas	0.9 L min^{-1} Ar
Make-up gas	0.8 L min^{-1} Ar
Sampling depth	5.4 mm
Detector	Dual (pulse and analog counting)
Dwell time/mass	6 ms
Laser parameters	
Wavelength	193 nm
Energy density	14 J cm^{-2}
Carrier gas	He (optimized to get the highest sensitivity)
Ablation style	Single spot
Ablation spot size	32 μm
Repetition rate	8 Hz
Laser pulse	480

Sensitivity of LA-ICP-MS was not only affected by the ICP-MS instrument, but also by sample position within the cell and laser focusing or imaging (Feldmann et al., 2006; Liu et al., 2007). The possible contributions of sample position and laser focusing or imaging to the time-drift can be corrected partially by normalizing to a major element (e.g., Si, Ca or Al). Although the drift of absolute sensitivity is not linearly correlated with time (Luo et al., 2007), relative drift of Si-normalized sensitivity varies linearly with time as a function of element mass (i.e., sensitivities of light elements decrease faster than the heavy elements) (Fig. 1), which is less likely to be produced during laser ablation or aerosol transportation and might be caused by ICP-MS instruments. Eggins et al. (1997) used multiple internal standards to surmount this problem in solution ICP-MS analysis. In this work, all count rates for each analysis were firstly normalized by Si (Al for spinel), and then a time-drift correction was applied using a linear interpolation (with time) for every twelve analyses (i.e., 2 NIST SRM 610+8 samples+2 NIST SRM 610) according to the variations of NIST SRM 610.

The USGS reference glasses BCR-2G, BHVO-2G and BIR-1G have chemical compositions of natural rocks (Rocholl, 1998; Jochum et al., 2000; Guillong et al., 2005; Jochum et al., 2005, 2006), and are homogeneous at the μm to mm scale with respect to major elements (RSD <1–2%) and most trace elements (RSD=1–4%) (Rocholl, 1998; Jochum et al., 2005), thus were used as reference materials for external calibration in this work. The element concentrations were calculated with Eq. (7). For a given element, high concentrations can be determined more precisely than low concentrations, and reference values of high concentrations are generally more accurate than low concentrations. Therefore, l values were calculated based on the concentration-weighted average (i.e., $l^i = \sum_{j=1}^{n} \left(\frac{C^i_{rm^j}}{cps^i_{rm^j}} \cdot \frac{C^i_{rm^j}}{\sum_{j=1}^{n} C^i_{rm^j}} \right)$, where n is the number of reference materials), which leads to the greatest reduction in uncertainty introduced by high uncertainties of those elements with low concentrations in the reference materials (e.g., Be, Rb, Mo, Cs, Th and U in BIR-1G). For comparison, quantitative calibrations were also conducted using a single reference material NIST SRM 610 by applying an AYCF and Ca standardization, respectively. An in-house program (ICPMSDataCal) was edited to perform the off-line selection and integration of background and analyte signals, and time-drift correction and quantitative calibration, which can be obtained from the author on request.

4. Results and discussion

4.1. Method uncertainties

In addition to the reference materials used for calibration and instrumental drift during LA-ICP-MS analysis, assumption of oxidation state for those elements having more than one oxidation state, and
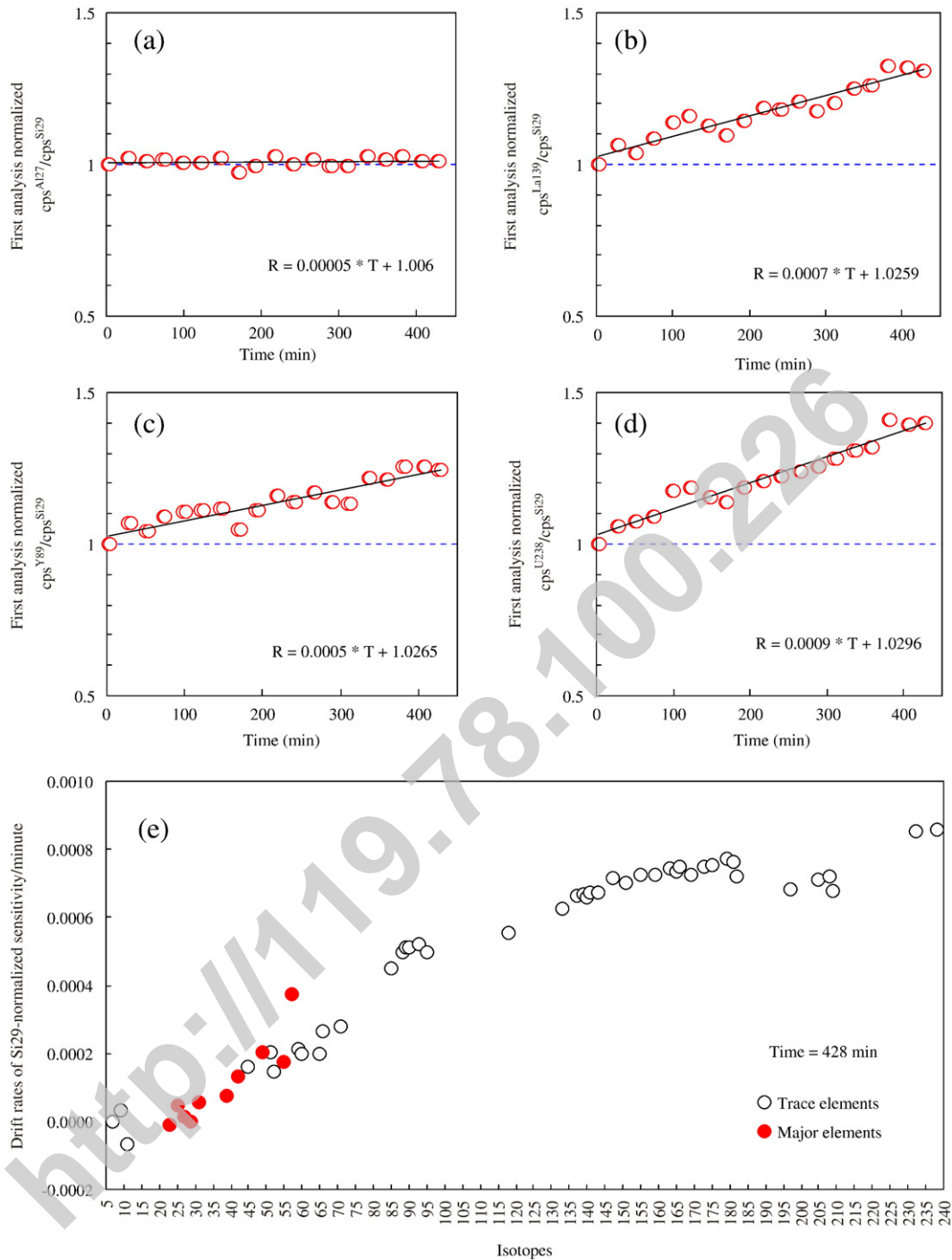
Fig. 1. (a–d) Time-dependent drifts of the mass discrimination for analyses of SRM 610. The equations are linear fits for variations of Si29-normalized sensitivity ratios (R) versus time (T). (e) Drift rates of Si29-normalized sensitivity of different isotopes, as defined by the slopes of linear fits for variations of Si29-normalized sensitivity ratios (R) versus time (T).

interferences of oxide and doubly charged ions on major elements would introduce uncertainty into the results in this method. RSDs of 49 elements in NIST SRM 610 and BCR-2G, BHVO-2G and BIR-1G show that, except for elements with low concentrations such as Li, Be, Bi, Cd, Cs, Mo, Sn, Ta and W, precision of their preferred values and thus homogeneity are comparable in respect of most elements. These suggest that, although uncertainties of LA-ICP-MS analyses are mainly caused by reference materials used for calibration (Luo et al., 2007), the results of most elements should not significantly change with the reference materials used for calibration.

Mass-dependent sensitivity variation would influence the results significantly, and is the principal limitation to quantitative analysis of low-mass elements (Eggins et al., 1997). In this work, all count rates for each analysis were firstly normalized by Si (Al for spinel), and then a time-drift correction was applied using a linear interpolation (with time) according to the variations of NIST SRM 610, which effectively reduce the uncertainty caused by instrumental drift. For example, relative standard deviation (RSD) of major elements decreased from 6.5–18.6% to 0.6–4.4% ($n=11$) for the MPI-DING and USGS glasses during a 428 min analysis (except for P_2O_5 in ATHO-G, GOR128-G and

GOR132-G). The high RSD of P_2O_5 in ATHO-G, GOR128-G and GOR132-G could imply heterogeneity in P_2O_5.

Uncertainty caused by assumption of oxidation state for those elements having more than one oxidation state depends on not only the assumption of oxidation state (e.g., $Fe^{2+}/\Sigma Fe$), but also concentrations of the elements. Fe and Mn are the only major elements that have two common oxidation states in silicates. The influence of Fe and Mn oxidation states on analysis of reference glasses has been discussed in detail by Guillong et al. (2005). Uncertainty introduced by oxidation states of Mn is negligible due to its low concentrations in the glasses and analyzed minerals. In this work, $Fe^{2+}/\Sigma Fe$ ratios of all reference glasses were assumed to be 0.5, which would result in a maximum relative error of 5% in the iron oxide concentration in the sample, and thus propagate to a maximum relative error of 5% multiplied by iron oxide percent of the total (i.e., 0.5% for a 10 wt.% iron oxide sample). $Fe^{2+}/\Sigma Fe$ in natural basaltic melt/glass varies from 0.57 to 0.89 (average = 0.74, n = 14) (Bonnin-Mosbah et al., 2001; Bouhifd et al., 2004; Métrich et al., 2006). Thus, a higher estimate of $Fe^{2+}/\Sigma Fe$ (e.g., 0.74) should be used for analysis of natural basaltic glass. The uncertainty introduced by an appropriate assumption of oxidation state of Fe in minerals is generally much less than the overall uncertainty in the determined concentration. For example, assuming of $Fe^{2+}/\Sigma Fe$ = 0.75 in the silicate minerals ($Fe^{2+}/\Sigma Fe$ ratios range commonly from 0.5 to 1 in olivine, pyroxene and garnet) could result in a maximum relative error of 0.64% for the mineral with the highest Fe concentration (e.g., garnet, $Fe_2O_3^{total}$ = 25.5 wt.%); Although $Fe^{2+}/\Sigma Fe$ (0.16–0.98; Brandon and Draper, 1996; Woodland et al., 2006) and iron concentration in spinel are highly variable, assuming of $Fe^{2+}/\Sigma Fe$ = 0.5 in the major Fe-bearing spinels would result in a maximum relative error of ~3.2%. Because $Fe^{2+}/\Sigma Fe$ ratios in minerals are generally fixed by crystal stoichiometry, the actual $Fe^{2+}/\Sigma Fe$ ratios can be calculated by recasting the measured mineral compositions with assumption of iron oxidation state in stoichiometric constituents. Thus, the uncertainty caused by iron oxidation state can be effectively decreased by recalculation with this calculated $Fe^{2+}/\Sigma Fe$ ratio.

Interferences of oxides and doubly charged ions on anyone element could theoretically cause uncertainty to the results of all elements present in the analyte. However, uncertainty caused by interference on trace elements is negligible because AYCF and l values in Eq. (7) are calculated based on concentration-weighted averages. Interferences caused by oxides (e.g., $^{24,25,26}Mg^{18,17,16}O$ on ^{42}Ca, $^{39}K^{16}O$ and $^{39}Ar^{16}O$ on ^{55}Mn, and $^{40}Ar^{17}O$ and $^{40}Ca^{17}O$ on ^{57}Fe) and doubly charged ions (e.g., $^{50}Ti^{2+}$ and $^{50}Cr^{2+}$ on ^{25}Mg, $^{58}Fe^{2+}$ and $^{58}Ni^{2+}$ on ^{29}Si) can be essentially limited by optimizing the carrier and make-up gas flows to reduce the oxide and doubly charged ion production. Furthermore, interferences caused by argon-based polyatomic ions (e.g., $^{40}Ar^{17}O$ on ^{57}Fe and $^{39}Ar^{16}O$ on ^{55}Mn) can be corrected by subtracting the count rates of gas blank. Kent and Ungerer (2005) confirmed that oxide production in LA-ICP-MS is related to the strength of M–O bond in the MO^+ ion, and $\log(MO^+/M^+)$ correlates linearly with M–O bond strength. The Th–O bond is among the strongest known for oxides (878.9 kJ mol^{-1}) and thus ThO^+/Th^+ production rate should represent the maximum oxide production rate expected for a given set of plasma conditions. On the other hand, Ca has a lower second ionization energy (11.87 eV) than Ti (13.58 eV), Cr (16.50 eV) and Ni (18.168 eV), and thus a higher doubly charged ion production rate than Ti, Cr and Ni. In this work, ThO/Th ratio was limited to 0.1–0.3% and Ca^{2+}/Ca^+ ratio to 0.4–0.7%, which implies that the interferences of polyatomic ions and doubly charged ions exist at a relatively low level. For example, contribution of MgO to ^{42}Ca is 1–3% for olivine which has the highest Mg/Ca ratio. To obtain more accurate Ca concentration in olivine, ^{43}Ca could be selected for analysis. Contributions of $^{50}Ti^{2+}$ and $^{50}Cr^{2+}$ on ^{25}Mg are respectively less than 0.01% and 0.72% for spinel, which has the highest (Ti, Cr)/Mg ratio. Although $^{58}Fe^{2+}$ and $^{58}Ni^{2+}$ contribute greatly to the counts of ^{29}Si for spinel (15–50%), this introduces negligible uncertainty to the other elements due to low Si concentration in spinel (<0.2 wt.%).

Some trace metal elements and anions (e.g., F, Cl, OH) that were not analyzed but present in the analyte would introduce uncertainty to the analyzed elements as well. The amount of uncertainty increases with the bulk concentrations of those unanalyzed elements. For hydrous minerals (e.g., amphibole), the results could be partially improved by normalizing to 100 wt.% minus the estimated concentrations of H_2O as used by Zajacz and Halter (2007) for analyses of silicate melt inclusions. Although uncertainty caused by those unanalyzed trace metal elements (e.g., PGE) is generally much less than the overall uncertainty in the determined concentrations due to their very low concentrations, all components should be measured in this method to obtain the most accurate result. The number of measured elements should be optimized according to the general knowledge about chemical compositions of the minerals because element concentrations vary significantly in different minerals.

On the other hand, deadtime related detector non-linearity, detector transition from pulse counting to analogue mode detection, and non-linearity of the analogue detection mode are also potentially detrimental to analysis when measuring isotopes of major elements (e.g. of Na, Mg, Al, and Si), as required by this method. Therefore, the detector response in its two modes of operation must be established for all analytes of interest for a particular experiment to ensure linearity of calibration. Fortunately, modern ICP-MS instruments mostly have the advantage of wide dynamic range by using a dual mode detector (e.g., nine orders of magnitude for Agilent 7500a), which can be easily established by the P/A (pulse/analogue) tuning.

4.2. Analyses of MPI-DING, USGS, NIST glasses using NIST SRM 610 as reference material for calibration

Regardless of the calibration strategy (applying Ca internal standardization or AYCF), the obtained SiO_2, MnO and K_2O concentrations determined by external calibration against NIST SRM 610 are usually higher, whereas TiO_2 and P_2O_5, Y, Zr, Nb and rare-earth element (REE) concentrations are lower than the recommended values for most of the MPI-DING reference glasses (Jochum et al., 2006) and USGS reference glasses (Jochum et al., 2005) (Fig. 2a and b). Although this systematic bias can be eliminated or reduced by internal standardization with Ca for MgO, Sr, REE, Hf, Ta, Pb, Th and U, large relative deviations from the preferred values still exist for most major elements (e.g., SiO_2, Fe_2O_3, MnO, Al_2O_3 and Na_2O) and some trace elements (e.g., Co, Ni, Cu, Zn, Ga and Rb) (Fig. 2a). Compared to the latest preferred values for the USGS and MPI-DING reference glasses, similar deviations have been previously observed for Co, Cu, Ni, Ga and Rb, and heavy rare-earth elements calibrated using NIST SRM 612 (Lahaye et al., 1997; Strnad et al., 2005) or SRM 610 as reference materials (Gao et al., 2002; Günther and Hattendorf, 2005). In contrast, when using NIST SRM 610 as reference material for external calibration, the accuracies of most elements obtained for NIST SRM 612 and 614 are generally better than 5–10% regardless of the calibration strategy.

The absorption behaviour of the NIST glasses is different when compared to the more opaque MPI-DING and USGS glass samples (Table A1 in Appendix), which leads to differences in the mass ablated and mass transported to the ICP. This effect has been discussed by Guillong et al. (2005) for the USGS GS series glasses using SRM 610 and BCR-2G for calibration. As previously shown, various mass loads of the ICP can lead to matrix effects (Kroslakova and Günther, 2007). Positive correlations between sensitivities and Fe concentrations were observed for most elements of the USGS and MPI-DING glasses, which implies a positive role of Fe in improving ablation due to higher absorption and smaller particle sizes, and therefore improved ionization efficiency (Kuhn and Günther, 2004; Guillong et al., 2005). However, it is worth noting that sensitivities of most elements in the Fe-poor NIST glasses are higher than those in the USGS and MPI-DING glasses (generally 10–30%). Here, we use the Ca-normalized sensitivity ratios (Ca-NSRs) between NIST SRM 610 and the other
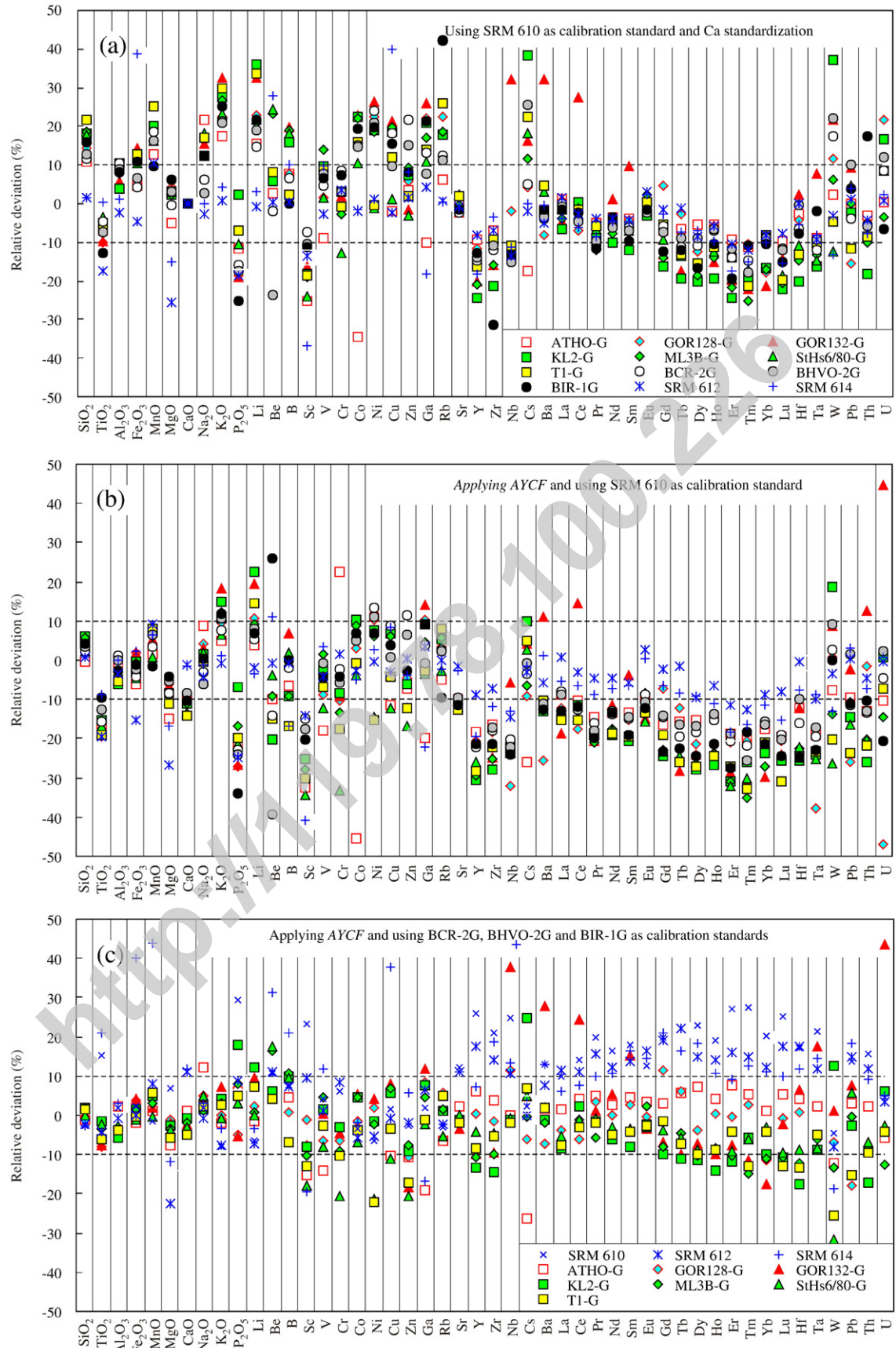
Fig. 2. Relative deviations (=100*(measured values−preferred values)/preferred values)) of element concentrations in the reference glasses calibrated with different strategies from the preferred values. (a) and (b) calibrated against NIST SRM 610 using Ca standardization and applying an AYCF, respectively. (c) Calibrated against multiple calibration standards (BCR-2G, BHVO-2G and BIR-1G) and applying an AYCF. The preferred values of element concentrations for the USGS and NIST reference glasses are from the GeoReM database (http://georem.mpch-mainz.gwdg.de/), and for the MPI-DING reference glasses from Jochum et al. (2006).
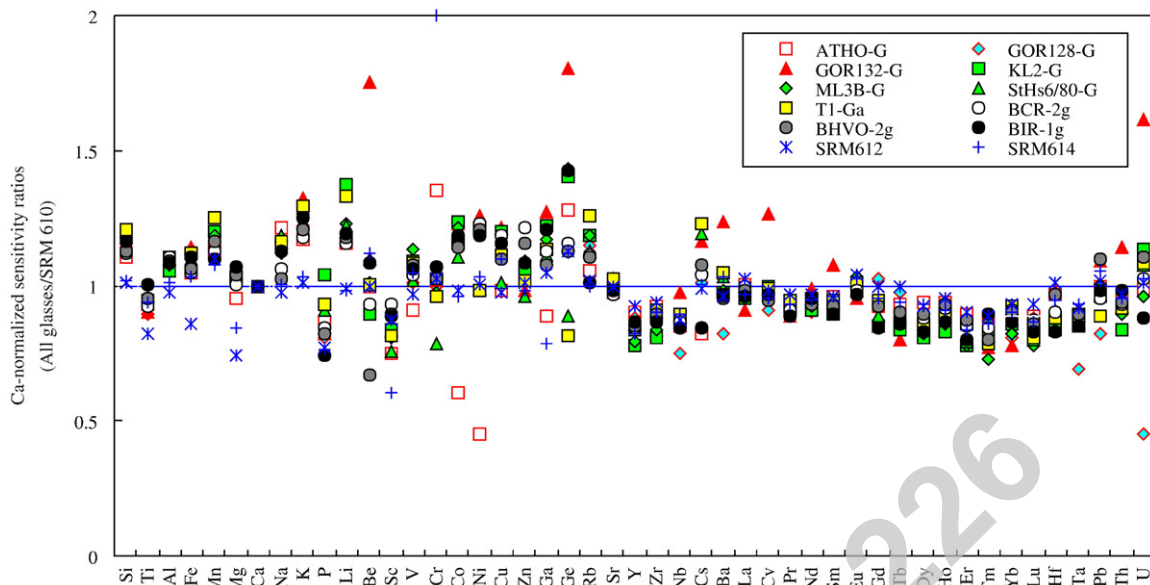
Fig. 3. Ca-normalized sensitivity ratios between the USGS, MPI-DING glasses and NIST SRM 610 (Ca-NSRs = Ca-normalized sensitivity of USGS and MPI-DING glasses/Ca-normalized sensitivity of NIST SRM 610).

glasses to evaluate the different element fractionations of the NIST glasses from the USGS and MPI-DING glasses (Fig. 3). In the case of an absence of any specific matrix-induced element fractionation, Ca-NSRs should be around 1. However, Ca-NSRs between NIST SRM 610 and the USGS and MPI-DING glasses vary significantly with elements. This implies that it is impossible to correct effectively the matrix effect using any element as the internal standard when calibrated using NIST SRM 610 as reference materials. For example, using ^{42}Ca as the internal standard, only those elements (e.g., Sr, Ba and Eu) with Ca-NSRs close to 1 can be corrected effectively. These observations clearly indicate that the specific matrix of the NIST glasses could induce remarkably different element fractionations from those glasses with natural compositions, which make the NIST glasses unsuitable reference materials for external calibration for analyses of natural silicate, as suggested by Jochum et al. (2007).

4.3. Analyses of MPI-DING and NIST glasses using USGS glasses as reference materials

By application of an AYCF and calibration using BCR-2G, BHVO-2G and BIR-1G as multiple reference materials, major elements and V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Cs, W and U in NIST glasses mostly match the working values within 10% uncertainty (Fig. 2c). However, a systematic bias was observed for element concentrations of Sr, Ba, Pb, Nb, Ta, Zr, Hf, Th and REE. The concentrations of these elements calibrated against multiple reference materials and applying an AYCF are generally ~5–25% higher than the working values, which is consistent with the previous observations that most of these elements in the USGS glasses calibrated against SRM 610 or 612 are generally lower than the preferred values (Lahaye et al., 1997; Gao et al., 2002; Strnad et al., 2005). Similarly, CaO values in NIST SRM 610 calibrated
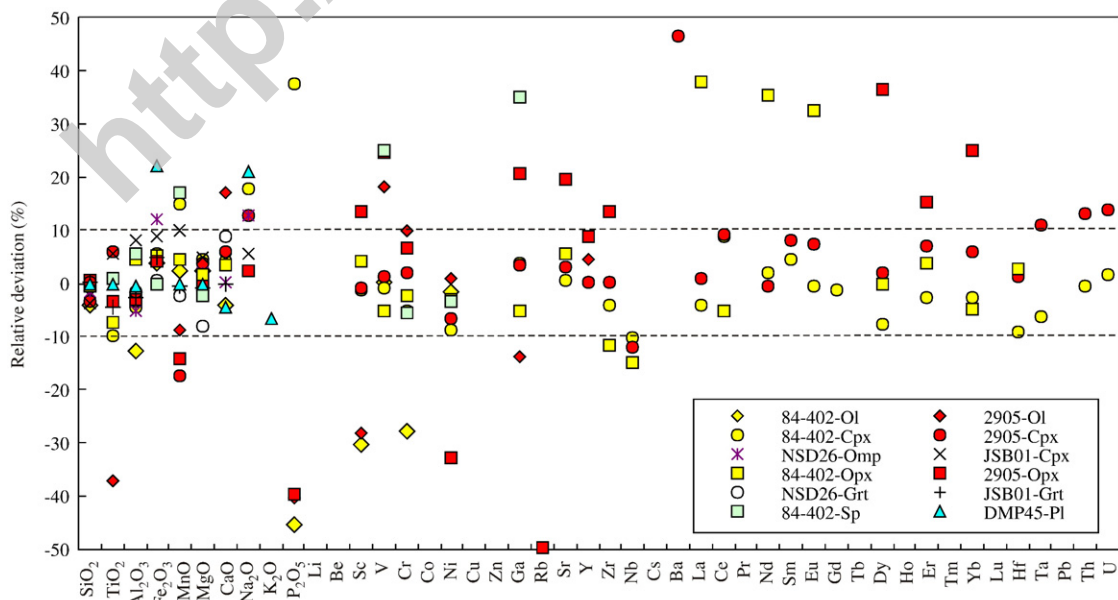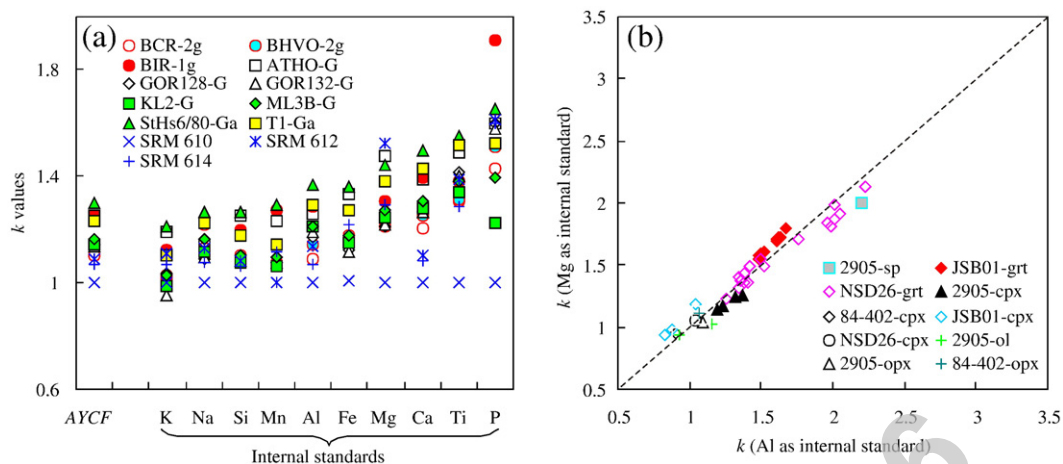

Fig. 4. Relative deviations of element concentrations in anhydrous minerals obtained in this work (applying an AYCF and using BCR-2G, BHVO-2G and BIR-1G as external calibration standards) from the results by EMP (major elements; this work and Eggins et al. (1998b)) and solution/laser ablation ICP-MS analyses by Eggins et al. (1998b).

Fig. 5. (a) Comparisons between k values calculated using different major elements as internal standards (Eq. (3)) and summed metal oxide normalization technique (AYCF, Eq. (6)). For comparison, NIST SRM 610 was used as external standard for calculations of k values. (b) Comparison between k values for the anhydrous minerals calculated using NIST SRM 610 as an external standard and Mg and Al as internal standards.

against multiple reference materials and applying an AYCF (12.5 wt.%) are always ~ 10% higher than the working values (11.5 wt.%). The same CaO concentration (12.5 wt.%) was also obtained by Halicz and Günther (2004) with liquid calibration.

The accuracies (expressed by relative deviation from the preferred values) of determined element concentrations for the MPI-DING glasses were significantly improved compared to the results calibrated against NIST SRM 610 (Fig. 2). The accuracies are better than 5% for SiO_2, Al_2O_3, Fe_2O_3, MnO and K_2O, and better than 10% for TiO_2, MgO, CaO, Na_2O and P_2O_5. Except for the transitional elements and those elements with concentrations close to detection limit (Table A1 in Appendix), the accuracies are generally better than 5–10% for trace elements (Fig. 2c). Large relative deviation (>20%) of a few trace elements could partially result from the large uncertainties of reference values (e.g., Ni, Ga, Mo, In, Cs in ATHO-G, and Zn, Sn in GOR132-G, and Mo, Sn in GOR128-G and T1-G) and counting statistics due to low concentrations (e.g., Cr in ATHO-G, and Nb, Ta, In, Sn, Ba, U in GOR132-G; Sn, Cs in KL2-G) (Fig. 2c and Table A1 in Appendix). It is worth noting that a systematic bias was still observed for REE in GOR132-G, KL2-G, ML2B-G, StHs6/80-G and T1-G, and the relative deviations are high up to 5–17% for the heavy rare-earth elements (Fig. 2c).

Because particle size distributions for samples with similar absorption and mass removal are similar and lead to equal vaporization of the particles in the ICP (Kuhn and Günther, 2004), the accuracy of natural samples (e.g., MPI-DING glasses) improved when using reference materials with natural compositions (e.g., USGS glasses) as external standards for calibration. However, due to the concentrations of some trace elements in reference materials with natural compositions are too low to yield sufficiently good measurement precisions, and thus counting statistics of these elements in reference materials (e.g., In, Cs and W in BCR-2G, BHVO-2G and BIR-1G) might influence the accuracy of the larger concentrations in the samples. This drawback can be remedied by using multiple calibration standards and concentration-weighted calibration as used in this work.

The contrasting results for MPI-DING glasses calibrated against SRM 610 and the USGS glasses could be well interpreted by particle size dependent elemental compositions (Kuhn and Günther, 2004). Kuhn and Günther (2004) indicated that Cu, Zn and Ga are significantly enriched relative to Ca within the smaller particles, while REEs are enriched in the larger particles. The lower Ca-normalized sensitivities of Cu, Zn and Ga but higher sensitivities of REEs in SRM 610 than in the USGS and MPI-DING glasses (Fig. 3) imply that laser-generated aerosol of the USGS and MPI-DING glasses could

contain more large particles than SRM 610 and would be less efficiently transported and/or vaporized. The systematic bias of REE in GOR132-G, KL2-G, ML2B-G, StHs6/80-G and T1-G calibrated against BCR-2G, BHVO-2G and BIR-1G could result from different particle size distributions between the analytes and the reference materials as well, which could be improved by optimizing the laser energy.

4.4. Analyses of anhydrous silicate minerals

Analyses of anhydrous minerals by applying an AYCF and calibration using BCR-2G, BHVO-2G and BIR-1G as reference materials give results that are mostly consistent with the EMP and solution-ICP-MS analyses (Fig. 4; Table A2 in Appendix). SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO and CaO generally match the EMP results within 5% relative deviation. Our analyses have ~ 10% higher Na_2O concentrations than the EMP analyses for clinopyroxene due to the fact that EMP determines a generally lower Na_2O concentration due to possible migration or volatilization of sodium during electron excitation (Butt and Vigers, 1977; Graham et al., 1984; Li, 1995). Because P_2O_5 concentrations (<0.02 wt.%) in these minerals were too low to be accurately determined by EMP, P_2O_5 concentrations show a significant difference between our results and the EMP analyses. SiO_2 concentrations in spinel obtained in this work are obviously higher than the EMP result, which could be attributed to the serious interferences of $^{58}Fe^{2+}$ and $^{58}Ni^{2+}$ on ^{29}Si.

Except for those trace elements with concentrations lower than or close to the detection limit (DL) (e.g., Ta, Pb, U and Th), trace element concentrations in clinopyroxenes are generally consistent with those obtained by Eggins et al. (1998b) within 10% relative deviation (Fig. 4). Trace element concentrations in olivine, orthopyroxene and spinel are mostly lower than or close to DL. Except for Ni, transitional element concentrations in olivine, orthopyroxene and spinel show relatively high deviations from the values obtained by Eggins et al. (1998b), which could be partially attributed to the chemical heterogeneity of these elements in the minerals.

These observations imply that, although the investigated minerals are generally quite different from the basaltic glass composition, calibration against BCR-2G, BHVO-2G and BIR-1G could provide satisfactory results. Thus, we speculate that this method might be successfully applied to other anhydrous silicate phases as well. Recasting the measured mineral compositions in stoichiometric constituents could be an effective method to evaluate the results for analyses of unknown minerals by this method.

4.5. Comparison between AYCF and k values calculated with internal standards

According to Eq. (2), the quantitative concentration of an element in LA-ICP-MS analysis can be obtained once the value of k is known. k can be calculated using an internal standard (Eq. (3)) or sum metal oxide normalization (AYCF, Eq. (6)). Using NIST SRM 610 as a reference material, k values of natural silicates calculated using different elements as internal standards vary significantly (Fig. 5). This variation was magnified by garnet and spinel (Fig. 5b), which implies that an artificial difference would be introduced when using different elements as internal standards. For example, the concentrations of trace elements calibrated using Ca as internal standard are higher than that calibrated using Si as internal standard about a factor of 1.07–1.26 for MPI-DING glasses using NIST SRM 610 as external standard. In this sense, the k value of AYCF is more robust than using a single internal standard, which is a "constant" for each analysis. Applying an AYCF can avoid artificial differences caused by using different elements as internal standard, and thus help ensure that the data reported by different laboratories are comparable.

On the other hand, AYCF of reference materials and samples were calculated based on the concentration-weighted average of all elements that can be determined in the analytes. Therefore, the uncertainties of elements in reference materials propagated to the combined uncertainty of the results by AYCF are also a concentration-weighted average. The data calculated using an AYCF were improved because the higher the concentration of one element, the smaller the uncertainties of the counting statistics and reference value. An exception is Na because EMP determines a generally lower Na_2O concentration for high-Na samples due to migration or evaporation of sodium during electron excitation (Butt and Vigers, 1977; Graham et al., 1984).

5. Conclusions

This work shows that the combination of the ablation yield correction factor (AYCF) and multiple calibration standards can be used to accurately analyze elements of anhydrous glasses and minerals by LA-ICP-MS without applying a previously known internal standard element. The results of MPI-DING glasses calibrated against multiple standards (BCR-2G, BHVO-2G and BIR-1G) and applying an AYCF are much better than those from using NIST SRM 610 as the calibration standard and Ca standardization. The contrasting element fractionations between the NIST glasses and those glasses with natural compositions could be interpreted by different particle sizes of the laser-generated aerosol. The results indicate that NIST SRM 610 is an unsuitable external standard for analyses of natural silicate. Applying multiple calibration standards and AYCF, the accuracies for the MPI-DING glasses are better than 5% for major elements, and better than 5-10% for most trace elements. Except for Na_2O and P_2O_5, major elements of anhydrous minerals are generally consistent with the EMP analyses within 5% uncertainty.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2008.08.004.

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